

SUBSTRATE, IN PARTICULAR GLASS SUBSTRATE, SUPPORTING AT
LEAST ONE STACK OF A PHOTOCATALYTIC LAYER AND A
5 SUBLAYER FOR THE HETEROEPITAXIAL GROWTH OF SAID LAYER

The present invention relates to substrates, such as
glass, glass-ceramic or plastic substrates, which have
10 been provided with a photocatalytic coating in order to
give them what is called an "antisoiling or self-
cleaning" function.

One important application of these substrates relates
15 to glazing, which may be applied in very many different
situations - from utilitarian glazing to glazing used
in domestic electrical appliances, from automotive
glazing to architectural glazing.

20 It also applies to reflective glazing of the mirror
type (domestic mirrors or driving mirrors) and to
opacified glazing of the lightened type.

Similarly, the invention also applies to nontransparent
25 substrates, such as ceramic substrates or any other
substrate that may in particular be used as
architectural material (metal, tiling, etc.).
Preferably, it applies, irrespective of the nature of
the substrate, to substantially flat or slightly curved
30 substrates.

Photocatalytic coatings have already been studied,
especially those based on titanium oxide crystallized
in anatase form. Their capability of degrading soil of
35 organic origin or microorganisms through the action of
UV radiation is very beneficial. They also often have a
hydrophilic character, allowing mineral soil to be

removed by spraying it with water or, in the case of outdoor glazing, by rain.

5 This type of coating exhibiting antisoiling, bactericidal or algicidal properties has already been described, for example in Patent WO 97/10186, which describes several embodiments thereof.

10 To exert its antisoiling function (hydrophilicity and destruction of organic contaminating chains), the TiO_2 must be at least partly crystallized in the anatase structure. Otherwise TiO_2 is not functional and requires a heat treatment after deposition, so as to acquire the crystallographic structure that makes it effective.

15 Thus, if the TiO_2 is deposited by a chemical vapor deposition (CVD) technique involving a high temperature, it has the correct structure spontaneously. If it is deposited cold (at room
20 temperature), especially by a vacuum deposition technique, it becomes functional only after a suitable heat treatment.

The object of the present invention is to propose a
25 solution for obtaining the correct state of TiO_2 without employing a heating step. However, such a heating step (toughening or annealing operation), envisaged in certain cases such as for safety applications or applications in which the surface of the glass has to
30 be hardened, is not excluded.

For this purpose, the present application proposes the deposition, just before deposition of the TiO_2 layer, of an underlayer that will provide an appropriate base for
35 correct growth of the TiO_2 layer (heteroepitaxial growth), this underlayer being advantageously deposited at room temperature and without requiring the substrate to be heated either.

International Application WO 02/40417 describes the deposition of a ZrO_2 underlayer followed by TiO_2 under very many possible conditions, with the need for
5 heating, without the preferential formation of anatase being demonstrated, the rutile form also being favored.

The first subject of the invention is therefore a structure comprising a substrate bearing, on at least
10 part of its surface, an antisoiling layer having a photocatalytic property, based on titanium dioxide (TiO_2) at least partly crystallized in its anatase form, characterized in that it includes, immediately beneath at least one TiO_2 layer, an underlayer (UL) having a
15 crystallographic structure that has assisted in the crystallization, by heteroepitaxial growth in the anatase form, of the TiO_2 -based upper layer, the photocatalytic property having been acquired without any heating step.

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The underlayer (UL) is in particular based on a compound crystallized in a cubic or tetragonal system and having a lattice cell dimension equal to that of TiO_2 crystallized in anatase form to within $\pm 8\%$,
25 especially to within $\pm 6\%$.

Preferably, the underlayer (UL) consists of ATiO_3 , A denoting barium or strontium.

30 The thickness of the underlayer (UL) is not critical. For example, thickness values of between 10 and 100 nm may be mentioned.

The substrate consists, for example, of a sheet,
35 whether plane or with curved faces, of monolithic or laminated glass, glass-ceramic or a hard thermoplastic, such as polycarbonate, or else consists of glass or glass-ceramic fibers, said sheets or said fibers

having, where appropriate, received at least one other functional layer before application of the underlayer (UL) (in the case of more than one layer, this may also be referred to as a multilayer stack).

5

The applications of the sheets were mentioned above. As regards the application of the fibers, mention may be made of air or water filtration, and also bactericidal applications.

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If the substrate is made of glass or glass-ceramic, at least one functional layer subjacent to the underlayer (UL) may be a layer forming a barrier to the migration of alkali metals from the glass or glass-ceramic. Such migration is liable to result from the application of temperatures in excess of 600°C. Such layers forming a barrier to alkali metals are known, and mention may be made of SiO₂, SiOC and SiO_xN_y layers, with a thickness for example of at least 50 nm, as described in PCT International Application WO 02/24971.

At least one functional layer subjacent to the underlayer (UL) may be a layer having an optical functionality (advantageously for adjusting the optics in reflection), a thermal control layer or a conducting layer.

The layers having an optical functionality are especially antireflection layers, light radiation filtration layers, coloration layers, scattering layers, etc. Mention may be made of layers consisting of SiO₂, Si₃N₄, amorphous TiO₂, photocatalytic crystallized TiO₂, SnO₂, ZnO.

35 The thermal control layers are especially solar control layers or what are called low-e (low-emissivity) layers.

The conducting layers are especially heating layers, antenna layers or antistatic layers, and arrays of conducting wires may be included among these layers.

5 To give an example, mention may be made of glass or glass-ceramic substrates, especially of the sheet type, that have received a layer acting as a barrier to the migration of alkali metals from the glass or glass-ceramic, followed by a monolayer, bilayer or trilayer
10 having an optical functionality.

The TiO_2 base layer consists of TiO_2 alone or of TiO_2 doped with at least one dopant chosen in particular from: N; pentavalent cations such as Nb, Ta and V; Fe;
15 and Zr.

According to advantageous features of the present invention:

- the TiO_2 layer has been deposited at room
20 temperature by vacuum sputtering, where appropriate magnetron and/or ion-beam sputtering;

- the underlayer (UL) has been deposited at room temperature by vacuum sputtering, where appropriate magnetron and/or ion-beam sputtering;

25 - ATiO_3 has been deposited at room temperature by vacuum sputtering, where appropriate magnetron and/or ion-beam sputtering, using ceramic targets chosen from ATiO_3 , ATiO_{3-x} where $0 < x \leq 3$, and ATi ,

the supply being a radiofrequency supply and
30 the atmosphere in the sputtering chamber containing only argon when ATiO_3 is used as target, the supply being a DC or AC supply and the reactive atmosphere in the sputtering chamber containing oxygen and argon when ATi or ATiO_{3-x} is used as target,

35 - the TiO_2 layer having been deposited in a following step in the same sputtering chamber.

The TiO_2 layer may be coated with at least one overlayer of a material that does not disturb the antisoiling function of the TiO_2 layer, such as SiO_2 .

- 5 The layers intended to be in contact with the atmosphere in the finished structure are, depending on the case, hydrophilic layers or hydrophobic layers.

10 The subject of the present invention is also the application of ATiO_3 to the formation of a layer for assisting in the crystallization, in the anatase form by heteroepitaxial growth, of an optionally doped ATiO_2 -based upper layer, A denoting barium or strontium.

- 15 The subject of the present invention is also a process for producing a structure as defined above, characterized in that an ATiO_3 underlayer, A denoting barium or strontium, is deposited on a substrate made of glass or glass-ceramic or hard polycarbonate-type
20 plastic, of the sheet type, or on glass or glass-ceramic fibers, followed by an optionally doped TiO_2 layer, at least one overlayer of a material not disturbing the antisoiling function of the TiO_2 layer then possibly being deposited where appropriate on this
25 TiO_2 layer.

The ATiO_3 underlayer (UL) and the TiO_2 layer may be deposited in succession at room temperature by vacuum sputtering, where appropriate magnetron and/or ion-beam
30 sputtering, in the same chamber, the targets used for depositing said underlayer being chosen from ATiO_3 , ATiO_{3-x} , where $0 < x \leq 3$, and ATi , the supply being a radiofrequency supply and the atmosphere in the sputtering chamber containing only argon when ATiO_3 is
35 used as target, the supply being a DC or AC supply and the reactive atmosphere in the sputtering chamber containing oxygen and argon when ATi or ATiO_{3-x} is used as target; and

the target used for depositing the TiO_2 being Ti or TiO_x , where $0 < x < 2$.

5 If the ATiO_3 is deposited by vacuum sputtering, the pressure may be between 10^{-1} and 2.5 Pa.

10 If the TiO_2 is deposited by sputtering, where appropriate magnetron and/or ion-beam sputtering, the supply is generally a DC or AC supply and the pressure is advantageously about 1-3 Pa.

15 According to the present invention, it is possible for a heat treatment step not to be carried out after the TiO_2 layer and, where appropriate, the overlayer(s) have been deposited.

20 If the coating of a glass or glass-ceramic substrate is carried out, it is possible, before the underlayer (UL) has been applied, to deposit at least one layer forming a barrier to the migration of alkali metals present in the glass or glass-ceramic to be deposited on the substrate, an annealing or toughening operation then possibly being carried out, after the TiO_2 layer and, where appropriate, the overlayer(s) have been
25 deposited, at a temperature of between 250°C and 550°C , preferably between 350°C and 500°C in the annealing operation, and at a temperature of at least 600°C in the case of the toughening operation.

30 The toughening or annealing operations may be carried out in cases where it will be desirable to improve the activity of the TiO_2 layer.

35 The possible constituents of the above barrier layers have been described above. Such layers may be deposited by sputtering, where appropriate magnetron sputtering, using known targets, (for example Al:Si in the case of an aluminum-doped SiO_2 layer), advantageously in pulsed

mode, whether AC or DC, at a pressure of 10^{-1} to 1 Pa and in gaseous argon/oxygen.

Before the ATiO_3 underlayer (UL) has been applied, at
5 least one functional layer chosen from layers having an optical functionality, thermal control layers and conducting layers may also be deposited, said functional layers being advantageously deposited by vacuum sputtering, where appropriate magnetron and/or
10 ion-beam sputtering.

The subject of the present invention is also single or multiple glazing comprising, respectively, one or more than one structure as defined above, both the TiO_2 -based
15 antisoiling layer and its associated underlayer (UL) being present on at least one of its external faces, the faces not having the TiO_2 -based antisoiling layer and its associated underlayer possibly including at least one other functional layer. These layers may be
20 chosen from those described above.

Such glazing is applicable as "self-cleaning" glazing, especially antifogging, anticondensation and antisoiling glazing, especially as architectural
25 glazing of the double-glazing type, automotive glazing of the windshield, rear window and side windows of automobiles, driving mirrors, glazing for trains, airplanes and ships, utilitarian glazing, such as glass for aquariums, shop windows, greenhouses, interior
30 furnishing, urban furniture (bus shelters, advertising panels, etc.), mirrors, screens for display systems of the computing, television or telephone type, electrically controllable glazing, such as electrochromic or liquid-crystal glazing, electro-
35 luminescent glazing and photovoltaic glazing.

The following examples illustrate the present invention without however limiting its scope.

Example 1 (according to the invention) : Glass/SiO₂/BaTiO₃/TiO₂ stack

5 The following successive layers were deposited on a glass sheet 4 mm in thickness:

- an SiO₂ layer 150 nm in thickness;
- a BaTiO₃ layer 10 nm in thickness; and
- a TiO₂ layer 100 nm in thickness.

10

The above three layers, SiO₂, BaTiO₃ and TiO₂, were deposited by magnetron sputtering under the following respective conditions:

15 - SiO₂ layer using an Al:Si target, with a supply in pulsed mode (change-of-polarity frequency: 30 kHz) at a pressure of 2×10^{-3} mbar (0.2 Pa), a power of 2000 W and 15 sccm of Ar and 15 sccm of O₂;

20 - BaTiO₃ layer using a BaTiO₃ target, with a radiofrequency supply, at a pressure of 4.4×10^{-3} mbar (0.44 Pa), a power of 350 W and 50 sccm of argon; and

- TiO₂ layer deposited using a TiO_x target with a DC supply, at a pressure of 24×10^{-3} mbar (2.4 Pa), a power of 2000 W, 200 sccm of Ar and 2 sccm of O₂.

25 Example 2 (according to the invention)

The same stack as in Example 1 was produced, except that the BaTiO₃ layer had a thickness of 20 nm.

30 Example 3 (comparative example): Glass/SiO₂/TiO₂ stack

The stack above was produced under the same conditions as in Example 1, except that the BaTiO₃ layer was not deposited.

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Example 4 : Evaluation of the photocatalytic activity

The photocatalytic activity of the TiO_2 layer of each of the stacks of Examples 1 to 3, and also of the TiO_2 layer of a stack sold by Saint-Gobain Glass France under the trademark "BiocleanTM" was evaluated, the evaluation having been performed without annealing and after annealing carried out under the following conditions: rise from room temperature to 500°C at a rate of $5^\circ\text{C}/\text{min}$; 2 hours at 500°C ; natural cooling.

The evaluation test was the stearic acid photodegradation test followed by infrared transmission, described in PCT International Application WO 00/75087.

The results are given in Table I.

TABLE I

Stack	SAT* without annealing ($\times 10^{-3}\text{cm}^{-1} \cdot \text{min}^{-1}$)	SAT* after annealing ($\times 10^{-3}\text{cm}^{-1} \cdot \text{min}^{-1}$)
Example 1 (invention)	9.7	40
Example 2 (invention)	9.2	32
Example 3 (comparative)	1.2	35

* Stearic acid test.